

Does exceptional viscous drag impede flow through a nano-sieve's pores?

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ABSTRACT

To address the concern that a material functionalized to reject dissolved ions may give rise to a highly viscous aqueous interphase within nanometers of its surface, we conducted and interpreted Interfacial Force Microscope measurements of the dissipative forces that resist motion of a tip parallel to a sample, in water. The results are consistent with earlier measurements where the tip approached the sample. They confirm that near hydrophilically functionalized surfaces, interphase viscosities more than 10^6 that of bulk water can be expected.

INTRODUCTION

The quality of a desalination membrane is measured by the purity and flux of the water that emerges downstream. Thus, in designing a synthetic desalination nano-sieve, an obvious question is how to functionalize its surfaces to reject ions to as large a distance as possible. If functionalization imposes a low ionic density within a distance w of a sieve's surfaces, then in the simplest model its pores can be as large as $2w$ in diameter without permitting many ions to pass (see Fig. 1). The flux of purified water then scales as w^2 , and there is no downside to making w as big as one can.

Appealing as this approach to better membranes may be, it is predicated on the assumption that functionalizing a surface has no countervailing impact on the viscosity of nearby water. The concern addressed herein is that it might, i.e., that within a few nm of an ion-rejecting surface, water will form an “interphase,” whose molecular structure gives rise to high viscosity. If this happened, downstream water would be pure. But, because of impeded transport, there would not be much of it. It would be possible to make a sieve with large holes, and not impair the downstream water. But flow of water through it would be “as slow as molasses.”

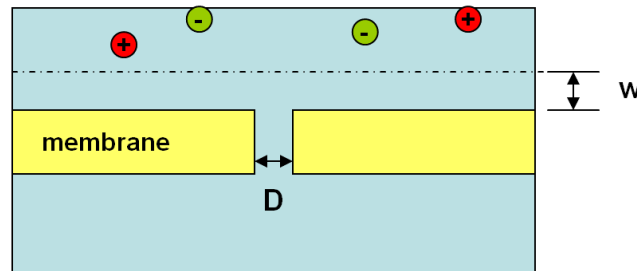


Figure 1. Schematic of a pore in a nano-sieve. If ions are rejected to a distance greater than w of the membrane surface, then pores of diameter $D < 2w$ will only pass pure water.

Behind this worry lie Interfacial Force Microscope (IFM)¹ measurements of the interphase viscosity at various functionalized surfaces.²⁻⁴ The IFM is a scanning probe instrument designed so that the delivery of charge to a pair of capacitor pads balances the force between a tip and a sample. (See Fig. 2.) The exquisite control this gives of the tip-sample separation allows one to measure the force that resists *drainage* of liquid from between a tip and a sample as the tip-sample separation is reduced at a fixed speed. It also permits a study of the resistance, in liquid, to motion of a tip *along* a sample.

In a first IFM-based drainage experiment, Kim, et al. coated a gold tip and sample with a self-assembled monolayer (SAM) comprised of long chain molecules, whose –OH head groups functionalized the coatings hydrophilic.² The remarkable result was that although the force resisting drainage was virtually not measurable for tip-sample separations greater than 5 nm, below this separation the force increased rapidly, and, characteristic of viscous drag, was greater for higher approach speed. (See Fig. 3)

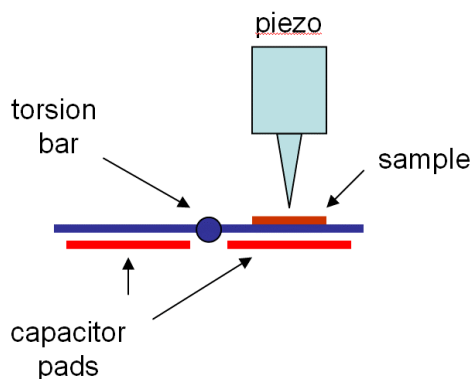


Figure 2. Schematic of an Interfacial Force Microscope. (See ref. 1) Delivery of charge to the capacitor pads balances the force acting between tip and sample.

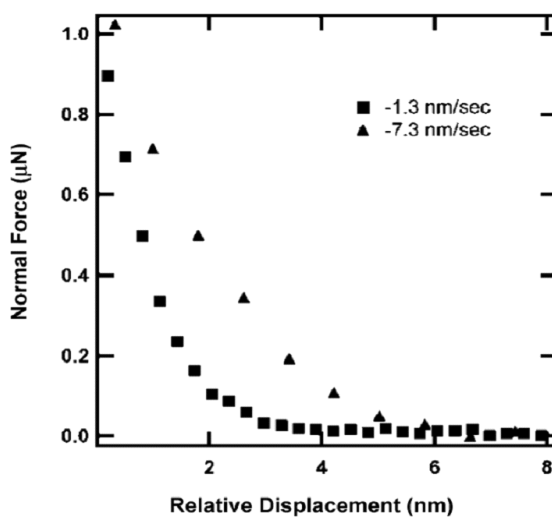


Figure 3. From ref. 2, the force resisting the approach of tip and sample, as a function of their separation and the approach speed.

The Kim, et al. data were analyzed using continuum, hydrodynamic lubrication theory, within a model in which tip and sample surfaces are each coated with an interphase layer of thickness, w , and viscosity, η .^{2,3} (See Fig. 4.) The bulk water beyond distance w from either surface is assumed to have zero viscosity. The sample surface, i.e., the locus of the ends of the SAM molecules, is taken to lie in the plane $z = 0$. The tip surface is a cylindrical, paraboloid. Thus, at a radial distance r from its central axis, the tip surface is at $z = D + r^2/2R$, where D , the minimum distance from its apex to the sample, is assumed to be much smaller than R , its radius of curvature.

Solution of the Navier-Stokes equations for this model, assuming a slow enough tip-sample approach speed, c , (= a few nm/sec) that terms quadratic in fluid velocity can be ignored, yields the formula for the force, F_{\perp} , resisting tip-sample approach,³

$$F_{\perp} \approx -6\pi \eta c (1 - D/2w)^2 R^2 / D \quad , \quad (1)$$

in which c and R are known, and D can be determined relative to a c -independent origin. Fitting Kim, et al.'s rather limited data set, the interphase viscosity was estimated to be some 7×10^7 that of bulk water.^{2,3}

The question is what to make of this remarkable result. At face value, it implies that functionalization of membrane surfaces to improve desalination efficiency is a more complicated matter than looking for ways to reject ions to larger distances. A more judicious approach is to step back and criticize the assumptions underlying the fit. They are that: 1) interphase water can be treated as an isotropic continuum, despite being only a few molecular layers thick, and bound to a hydrophilic surface, 2) surface roughness of the tip and the sample can be ignored, 3) the boundary between the interphase water and the bulk liquid can be treated as spatially sharp, and flat, and 4) the details of the OH-terminated tri(ethylene glycol) undecylthiol [or "EG3OH"] hydrophilic SAMs on the Au surfaces can be ignored, apart from a zeroth order effort to account

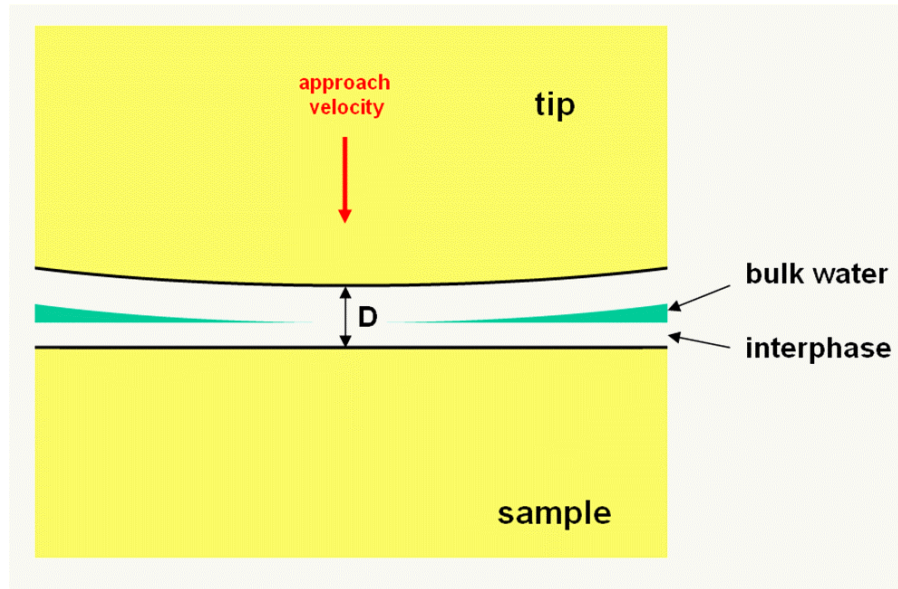


Figure 4. Schematic of drainage experiment. The tip surface lies at $z = D + r^2/2R$, where r is the radial distance from the central axis. The sample surface is at $z = 0$.

for their elastic compliance.²

Beyond the perhaps unjustified use of these approximations, there is no current microscopic explanation for the large viscosity. Neutron scattering experiments imply that the interphase density is virtually identical to that of bulk water.⁵ X-ray scattering shows no evidence for formation of more than one or two ordered water-molecule layers at oxide surfaces.⁶ The idea that confinement between tip and sample causes the water to crystallize into an “ice” layer⁷ is belied by an interphase viscosity that, though large, is some 7 orders of magnitude smaller than the viscosity of ice just below the freezing point.⁸ Thus, one may imagine that interphase water is characterized by an enhanced formation of transient clusters. But, though there is no evidence against that hypothesis, nothing directly supports it either.

FRICITION EXPERIMENTS

Faced with these good reasons for doubt, we undertook to extend the IFM data set to measurements of the force resisting tip drag *along* sample surfaces.⁴ This has immediate advantages: 1) In contrast to the drainage experiment, the effects of any “body forces” i.e., forces at a distance between tip and sample, like van der Waals, are eliminated from consideration, because the tip-sample distance is fixed. 2) The same applies to the concern that elastic compliance of the SAM layers played a role in producing what looks like a huge interphase viscosity. In addition, 3) the drag experiment provides an internal consistency check. Does the effective viscosity in this case equal what is found in a drainage measurement, using the same tip and sample preparations?

Thus, IFM drag measurements (See Figs. 5 and 6) have been conducted, and not just for EG3OH-coated Au tip and sample, but also, in an effort to eliminate the effects of SAM elasticity entirely, for a W tip on a Si sample, both hydroxylated by dipping in H₂O₂. To enable

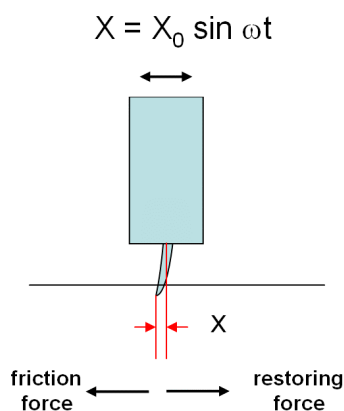


Figure 5. Schematic of drag experiment. As the piezo on which the tip is mounted is caused to oscillate, the tip is bent by frictional resistance (in the present case, by viscosity). Balancing the friction against the tip’s elastic restoring force yields a forced oscillator equation. From its solution, one derives the dissipative force, i.e., the measured force 90° out of phase with the piezo’s oscillation.

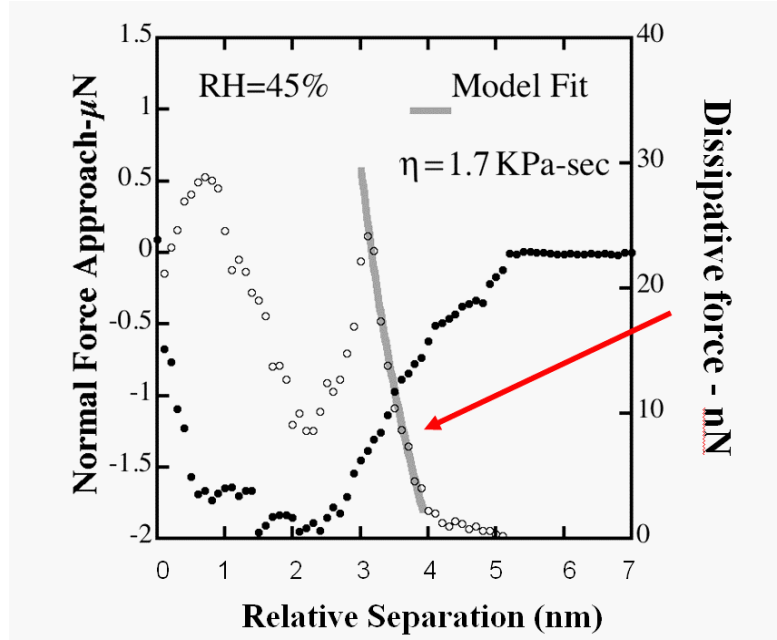


Figure 6. After Ref. 4. Results of a drag experiment involving a W tip and a Si sample, both hydroxylated by dipping in H_2O_2 . As the tip approaches the sample in a chamber maintained at 45% relative humidity, a pure water meniscus condenses from the vapor when the tip-sample separation is ~ 5 nm, as evidenced by the appearance of an attractive force (black dots). At this separation, a frictional resistance (open circles) is first observed, but is small. At ~ 4 nm separation, the frictional force begins a dramatic increase, described extremely well by the Navier-Stokes solution (grey line) discussed in the main text. The fit allows a value of the viscosity to be extracted, which is more than 10^6 larger than that of bulk water. At a tip-sample separation somewhat above 3 nm, the hydrodynamic fit is no longer valid. The significance of this behavior remains to be understood, both physically, and regarding its implications for filtration. Experiments conducted with the same tip and sample in a droplet of 18 Mohm/cm water, instead of a condensed meniscus, yield essentially the same viscosity.

fits to the new data, we once again applied hydrodynamic lubrication theory.⁹ The model used was identical to that for the drainage experiment, apart from changing the tip's velocity from normal to parallel to the sample surface.

HYDRODYNAMIC THEORY AND COMPARISON TO EXPERIMENT

The asymmetry inherent in this change complicates the solution of the Navier-Stokes equations. Nevertheless, the typical scaling behavior of hydrodynamic theory makes it possible to present the solution simply. In particular, the force, $F_{||}$, resisting tip motion along the sample, is given by,

$$F_{||} = -2\pi\eta cR \Phi(D/2w) \quad , \quad (2)$$

where the smoothly varying function Φ is well approximated by $-\ln(D/2w)$, if $D/w > 1$.⁹ Thus, one has an analytic expression for the drag force, provided the tip-sample distance is greater than the width of a single interphase, namely,

$$F_{||} \approx 2\pi \eta cR \ln(D/2w) \quad . \quad (3)$$

When the tip and sample interphases barely overlap, i.e., when $2w/D$ is just a bit larger than 1, the logarithm of eq. (3) can be expanded, yielding the asymptotic expression,

$$F_{||} \approx -2\pi \eta cR (2w/D - 1) \quad . \quad (4)$$

This result is of interest in comparison with the drainage result of eq. (1). Given the assumption that $R \gg D$, and in the experiments, typically, R was of order a micron, while D was a few nm, F_{\perp} is expected to be much larger than $F_{||}$ assuming equal tip speeds. Alternatively, the drag experiment has to be run with the tip moving roughly 100 times faster than in the drainage mode, to yield an equally large frictional resistance. Satisfyingly, this turns out to be true in the experiments.^{1,4} Indeed, no signal is detected in a drag experiment if the tip is moving appreciably slower than a $\mu\text{m/s}$.

Fits of Eq. 3 to drag force measurements are shown in Fig. 6. As in the earlier drainage study, the agreement of data and hydrodynamic prediction is excellent, although in this case the agreement only lasts as long as the tip is not “too close” to the sample. Restricting attention to the regime in which the fit is good, the viscosity extracted from the data once again is more than 10^6 greater than that of bulk water. The agreement with the drainage result is imperfect, but likely as close as should be expected, considering the limited measurements of Ref. 1.

Similarly good fits (not shown), yielding comparably large interphase viscosities, were obtained from data for an Au tip and sample, both coated with $-\text{COOH}$ terminated SAMs. The conclusion thus seems inescapably that viscosity is drastically enhanced within nanometers of hydrophilic surfaces.

FUTURE DIRECTIONS

As noted, when the tip-sample separation reaches what looks to be a “critical value,” the hydrodynamic model appears to break down. Future efforts are aimed at interpreting this surprising result. Does it mean that there is a critical strain rate above which interphase viscosity decreases? Does it signal the regime in which continuum theory no longer applies? And are there implications for using functionalized surfaces to build efficient desalination membranes? These are the questions we hope to answer.

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